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(54) **Rinsing and cleaning method for industrial goods.**

(57) A method for rinsing goods which have been cleaned in an aqueous degreasing or cleaning bath is provided wherein in a closed system the impurities and other agents are rinsed off the surfaces of the goods and organic matter is degraded by microorganisms contained within the rinse system. Further, a method for cleaning goods is provided which comprises cleaning these goods in a cleaning or degreasing system (either conventional or biologically active) followed by rinsing them in a closed system wherein during the rinsing step the cleaning solution and impurities are rinsed off the surfaces of the goods and organic matter is degraded by microorganisms contained within the rinse system.

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Industrial goods are cleaned and degreased during and after manufacturing, in preparation for surface treatment processes, in connection with their repair or maintenance, and frequently during their lifetime in order to preserve their appearance and functionality.

Cleaning systems used for such purposes are known. Former systems usually involved organic solvents but their use is being restricted progressively because of their adverse environmental and human health effects. Cleaning systems based on water solutions are used increasingly. Such aqueous solutions are either alkaline, using sodium or potassium hydroxide, or acid, using phosphoric or other acids, plus other inorganic and/or organic components for best effectiveness, and they are being operated more or less hot.

The solutions, when used, become more and more contaminated with the oils and greases which they remove from the goods. In order to eliminate these impurities, the cleaning solutions may be skimmed, filtered, centrifuged or otherwise treated to separate and remove the impurities and thus extend their functional life. The separated impurities must be taken care of, preferably with minimum environmental impact. Furthermore, those impurities that are not or cannot be separated from the cleaning solution remain to be taken care of by periodical disposal of the contaminated cleaning solution, preferably also with minimum environmental impact. Finally, the impurities are being carried into pickling solutions or other treatment solutions which follow in the treatment path of the goods. Pickling solutions contaminated with such impurities are less effective and are to be replaced rather often, causing even more waste to be discharged as well as high costs. Even if the goods do not pass through further treatment steps the degreasing solution with its full organic content on their surface must still be taken care of.

In the European patent application 88 850 310.9, a method of cleaning objects has been proposed wherein the objects or goods are degreased and the degreasing solution is continually treated biologically to eliminate the oils and greases which are removed from the goods as they are being cleaned, and which contaminate the solution. The method is characterized in that microorganisms perform biodegradation of organic substances, separately from or simultaneously with the cleaning. This biological degradation results in overcoming part of the disadvantages of the conventional degreasing bath techniques since oil and grease content of such a degreasing bath is being kept to a minimum which is the continual resulting balance between input and degradation. Further, it is effective in producing predominantly inorganic sludge in greatly reduced quantities the disposal of

which is more readily possible. The bacteriological activity is controlled in such a way that it is concentrated on the oil and grease while avoiding degradation of the degreasing agents, e.g. tensides and emulsifiers. This is necessary because the effectiveness of the bath is dependent on the concentration of the degreasing agents. Even though this method effectively reduces the transport of oil and grease into the pickling or other treatment solutions, the carryover of organic cleaning agents is inevitable. The latter, when adhering to the surface of the goods to be treated, interfere with the economical reprocessing of spent pickling solutions and with the disposal of treated waste waters.

It has been proposed to spray water over the goods further to be treated in order to rinse off cleaning or degreasing liquid. However, even if a rinse bath is used to catch the contaminated solution the rinse bath itself must be treated or disposed of with similar associated environmental impact. As the rinse bath in turn is more or less contaminated with the degreasing solution, depending on the frequency of its treatment, contaminated degreasing solution is always carried beyond the degreasing and rinse unit and into other process units, e.g. the unit for pickling the goods.

The problem of the present invention is to provide a method for cleaning goods further to be processed in pickling or other treatment solutions wherein the carryover of impurities into the said solutions is minimized in order to ensure effectiveness of the pickling or other treatment baths and to minimize costs in recycling and disposing of the exhausted solutions.

It is therefore an object of the present invention to provide a method for rinsing goods which have been cleaned in a degreasing or cleaning bath (either a conventional or a biological bath), wherein in a closed system the impurities and other agents are rinsed off the surfaces of the goods and organic matter is degraded by microorganisms contained within the rinse system.

It is further an object of the present invention to provide a method for cleaning goods which comprises cleaning these goods in a cleaning or degreasing system (either conventional or biologically active) followed by rinsing them in a closed system wherein during the rinsing step the impurities are rinsed off the surfaces of the goods and organic matter is degraded by microorganisms contained within the rinse system.

The present invention eliminates organic matter in a rinse stage following degreasing, into which the degreasing solution has been carried on the surface of the goods.

The advantage of eliminating the used solution in the rinse bath in which the degreasing solution is washed off the goods lies in minimizing the trans-

port of organic materials into other processes and it lies in not treating and/or discharging large quantities of rinse water containing organics with associated environmental impact.

### Detailed description of the invention

Following the degreasing step, the rinse system provides a washing step wherein the adhering degreasing solution is washed off the goods and degradation of organic matter (tensides, emulsifiers, remaining oil and grease) is effected by support of microorganisms. The rinse system of the present invention utilizes the rinse liquid in a bath into which the cleaned and degreased goods are immersed. Alternately, the rinse liquid is sprayed over the goods to be rinsed within a containment and collecting system. In either case, the rinse liquid is in a closed system in contrast to an open flow through rinse system.

The used degreasing solution is eliminated in this rinsing system by biological degradation using microorganisms which digest oils, greases, tensides and emulsifiers. This biological treatment may be accomplished in a continuous process in which the degreasing solution transferred on the surface of the goods into the rinse bath is washed off and treated.

The solution which is being removed from the degreasing bath is replaced by fresh degreasing solution in order to maintain degreasing effectiveness at all time.

The microorganisms used for biological degradation in the rinse stage of the the present invention have a biological activity which is developed and supported by providing suitable pH and temperature conditions, and preferably providing nutrients and oxygen. In this way, organic materials such als oils, greases, tensides, and emulsifiers are degraded and thus eliminated. This means that the condition in the rinse bath is maintained such as to promote and sustain the desired biological activity which degrades the oils, greases, and other organic impurities including tensides and emulsifiers carried into the rinse liquid through the degreasing solution and removed from the surface of the goods.

The pH of the rinse system may be controlled by its continuous measurement and by the dosage of alkaline or acid additives, e.g. solutions containing phosphoric acid or sodium hydroxide. These additives can be dosed as needed, preferably together with the specific nutrients for the sustenance of the cultures best suited for the organic materials to be degraded, and other biologically degradable components for the conditioning of the rinse system. The pH value is maintained near of slightly above neutral (preferably between 5.5 and 8.5,

more preferably about 7 to 8).

The biological activity is stimulated and supported by keeping the rinse water temperature preferably between 30 and 60 °C which may be accomplished by heating the bath as needed. Usually, a temperature of between 35 and 45 °C is most preferred, but various soil colonizing bacteria grow at temperatures from near the freezing point up to about 35 °C. On the other hand, thermophilic organisms may be used in the present method, and therefore temperatures up to the boiling point may be selected.

The biological activity is preferably stimulated and supported by nutrients. Even in case no organic material is carried into the rinse system, nutrients sustain a minimum population of microorganisms. Nutrients added are preferably those which are known to be best suited in supporting growth of the microorganisms used. On the other hand, selection of specific nutrients may control the growth of microorganisms in such a way that growth of undesired bacteria is suppressed. The nutrients may be selected from a variety of substances known in the biological sciences, from carbon and nitrogen sources, phosphorus and/or sulphur containing compounds, inorganic salts, and the like. Usually, the nutrients are selected from the group comprising sugars, amino acids, ammonium salts of organic and inorganic acids, phosphorus containing compounds, sulphur containing compounds, and derivatives of carbonic acid. Preferred examples for such compounds are glucose, glutamate, glutamic acid, ammonium hydroxide, ammonium chloride, ammonium propionate, phosphatides, thioglycolates, urea and the like. Depending on the dosage of alkaline or acid additives, respectively, in order to maintain the proper pH value, the nutrients may be suitably selected, e.g. ammonium hydroxide or ammonium chloride, respectively. The selection will also be dependent on the oils, grease, and other organic and inorganic compounds which have been carried over into the bath together with the goods to be treated. Of course, addition of nutrients may be omitted in case the organisms are fully supplied by the impurities.

Oxygen is supplied in order to maintain an aerobic activity by injecting air or another oxygen containing or releasing gas into the solution.

Microorganisms enter the rinse system with the oils and greases; however, they may be added prior to or during the operation of the rinse bath, e.g. by adding samples from other biologically active baths. Some microorganisms are usually found in mineral oils and therefore applicable in the present invention. Microorganisms involved in the bio-activity include such bacteria belonging to strains of e.g. Saprophytes, Pseudomonas, Kleb-

siella, Thiobacillus, Acetococcus, Acinetobacter, Corynebacterium, Nocardia, Xanthomonas, Flavobacterium, Mycobacterium and the like. Of course, other suitable natural as well as genetically tailored microorganism which e.g. could additionally degrade silicon compounds including silicones may be used as well. Preferably, the organisms used are those introduced with the goods to be treated. Additionally or alternately, the bioactivity of the rinse system is initiated or restarted by introducing sludge or liquid taken from the same or another rinse system run previously which contains the respective microorganisms.

The rinse system may be kept clean and free from residue (including dead bacteria) and inorganic suspended matter (e.g. sand, soil, rust, scale, etc.) by collecting and removing sludge through a suitable sludge separator. This may be accomplished using a settler or filter or by other appropriate means and measures known per se.

The rinse bath may be in the form of a spray chamber with collecting tank and pump for circulating and spraying the solution onto the goods to be rinsed.

The transfer of degreasing solution into the rinse bath may be augmented by continuous or discontinuous transfer of used solution into the rinse bath. This may be desired when the goods are relatively heavily oiled and the degreasing solution becomes strongly contaminated.

The rinse effect may be further improved by using a second or even more rinse stage(s) in succession. The solution from the first rinse stage is carried into the second or next rinse stage in the same way as the solution from the degreasing stage is carried into the first rinse stage. The result is a greater reduction in the level of residual organic content. This may be desirable when the goods are relatively oily and large quantities of oil must be degraded.

Prior to the rinsing step, the goods are usually cleaned in a disposable degreasing bath. This is usually an aqueous system comprising e.g. either alkaline or acid solutions, with or without further organic and/or inorganic components, especially anionic or nonionic tensides and/or emulsifiers depending on the type and condition of the oil, grease or other impurities to be removed from the goods. Such degreasing baths accumulate and pass on the emulsified oil and grease. A typical degreasing solution contains tensides, emulsifiers, caustic soda and other inorganic salts according to the state of the art. It has a high temperature as needed for effective degreasing (usually 50 to 60 °C or higher, but lower temperatures are possible) and it is usually alkaline (has a high pH value), but it may be acid. Degreasing systems have been described and used previously. They may be re-

cycled as disclosed in US Patent 4 124 504 or European patent application 83 112 585.1.

Alternately, the degreasing stage may be a biologically active bath as described above or it may include a second or even more degreasing bath(s) at least one of which is biologically active. In this case, microorganisms, pH and nutrients have to be selected so that oil and grease are degraded in situ while the tensides and emulsifiers used are maintained. This may be achieved by using pH values in the range of 8.5 to 9.7. For example, the bio-active solution is held at 35 to 40 °C and the pH at about 9. It is aerated. Nutrients as well as tensides and emulsifiers are added. The bio-activity is controlled to degrade oils and greases but not the tensides and emulsifiers. This two-stage or multiple stage degreasing process can be advantageous when the goods are relatively heavily oiled and the degreasing solution becomes strongly contaminated.

The degreasing step may be run with hot or cold solutions. Consequently, the goods to be rinsed and/or the degreasing solution imported into the rinsing system may be hot or cold. The heating and the dosage equipment of the rinse system are designed for all possible production conditions.

#### EXAMPLE 1:

A degreasing system using a hot alkaline degreasing bath and a biologically active rinse bath in which the degreasing solution is washed off the cleaned goods and degraded in a continuous process.

The degreasing bath is maintained at about 60 °C. The degreasing product contains tensides and emulsifiers, caustic soda and other inorganic salts according to the state of the art.

The goods are immersed and left in the degreasing bath for a period of 10 to 30 minutes, depending on the severity of their contamination with oil, grease, and other organic impurities. The bath is an alkaline solution with a pH of close to 14, although lower pH-values as well as acid degreasing baths are also commonly used and are possible in this connection. The oils and greases are saponified and/or emulsified and become mixed with the bath solution.

Following this treatment the goods are withdrawn from the degreasing bath and immersed in the rinse bath. The degreasing solution which is wetting the surface of the goods and which contains the impurities is rinsed off the goods and mixed with the rinse water.

The rinse bath is maintained at 40 to 45 °C by circulation through a separate heat exchanger or heater, although other means of heating such as with immersion heaters are possible. The bath is

aerated to provide oxygen for the microorganisms by blowing air through submerged nozzles. The pH of the rinse water is kept close to 7 by the controlled dosage of a caustic or an acid solution containing sodium hydroxide and phosphoric acid, respectively, although other substances are possible (e.g. potassium hydroxide).

The degreasing solution and the impurities that are imported into the rinse bath are being degraded biologically. They are the intended nutrients for the microorganisms in the rinse bath. The amount of impurities in the rinse bath at any given time depends on the rate of import. During non-production periods the concentration of impurities decreases.

The pH-control solutions contain glucose and urea which stimulate the biological activity. These nutrients support the activity during non-production periods.

The degreasing bath is constantly renewed by continuous partial transfer into the rinse bath and by the addition of new product in accordance with the consumption. Thus, the disposal of the degreasing bath occurs through biological degradation in the rinse bath.

Non-degradable impurities such as sand, rust, and other insolubles are separated by circulating the rinse bath through a settler. Besides such inorganic impurities there are also dead bacteria in the sludge. This small quantity of sludge is the one waste which needs to be disposed of.

The advantages of the above rinse process are the minimizing of wastes which must be disposed of and/or which are transported beyond the rinse bath. The benefits are reduced waste and cost.

#### EXAMPLE 2:

Biologically active rinse bath in connection with a biologically active degreasing bath. The degreasing solution together with the impurities is rinsed off the goods and degraded biologically in the rinse bath.

As in example 1, the goods are immersed and left in the degreasing bath for a period of 10 to 30 minutes, depending on the severity of their contamination with oil, grease, and other organic impurities. The bath is slightly alkaline with a pH of about 9 and a temperature of 35 to 40 °C.

Following this treatment the goods are withdrawn from the degreasing bath and immersed in the rinse bath. The degreasing solution which is wetting the surface of the goods and which contains the impurities is rinsed off the goods and mixed with the rinse water.

The conditions of the biologically active degreasing and rinse baths are maintained as in example 1, including heating, aeration, pH-control, and

the removal of sludge. The nutrients added together with the pH controlling agents are glutamate/glutamic acid and ammonium hydroxide/chloride.

The advantages and benefits are the same as in example 1.

The advantages of the present invention as disclosed above are a combination of environmental, operational and economic benefits; firstly, because the organic impurities do not need to be separated from the degreasing or cleaning solution, thus presenting a disposal problem, secondly, because the contaminated cleaning solution does not have to be disposed of and to be renewed, and, thirdly, because tensides and organic impurities in the cleaning solution on the surface of the goods are not being carried into the subsequent treatment steps.

#### Claims

1. A method for rinsing goods which have been cleaned in an aqueous degreasing or cleaning bath wherein in a closed system the impurities and other agents are rinsed off the surfaces of the goods, **characterized in that** organic matter is degraded by microorganisms contained within the rinse system.
2. A method for cleaning goods which comprises cleaning these goods in a cleaning system followed by rinsing them in a closed system wherein during the rinsing step the cleaning solution and impurities are rinsed off the surfaces of the goods, **characterized in that** organic matter is degraded by microorganisms contained within the rinse system.
3. A method as claimed in claim 1 or 2, **characterized in that** the rinse step is operated by immersing the goods in a bath.
4. A method as claimed in claim 1 or 2, **characterized in that** the rinse step is operated by spraying the goods with rinse liquid and collecting the rinse liquid.
5. A method as claimed in any of claims 1 to 4, **characterized in that** the temperature of the rinse liquid is between 35 and 45 °C.
6. A method as claimed in any of claims 1 to 5, **characterized in that** the pH of the rinse liquid is maintained between 5.5 and 8.5, preferably at or near neutral (about pH 7 to 8).
7. A method as claimed in any of claims 1 to 6, **characterized in that** nutrients selected from

the group comprising carbon, nitrogen, phosphorus, sulphur and inorganic salts are added to the rinse liquid.

17. A method as claimed in any of claims 2 to 16, **characterized in that** cleaning the goods is performed in two or more degreasing baths.

8. A method as claimed in claim 7, **characterized in that** the nutrients are selected from the group comprising sugars, amino acids, ammonium salts of organic and inorganic acids, phosphorus containing compounds, sulphur containing compounds, and derivatives of carbonic acid. 5  
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9. A method as claimed in claim 8, **characterized in that** the nutrients are selected from glucose, glutamate, glutamic acid, ammonium hydroxide, ammonium chloride, ammonium propionate, phosphatides, thioglycolates, and urea. 15
10. A method as claimed in any of claims 1 to 9, **characterized in that** the rinse liquid is supplied with oxygen. 20
11. A method as claimed in any of claims 1 to 10, **characterized in that** the required microorganisms enter the rinse system together with the oil/grease attached on the surface of the goods. 25
12. A method as claimed in any of claims 1 to 11, **characterized in that** microorganisms which are able to degrade organic compounds are additionally incorporated into the rinse liquid. 30
13. A method as claimed in claim 12, **characterized in that** sludge or liquid separated from the same or another rinse system run previously and containing the said microorganisms is added to the rinse liquid. 35  
40
14. A method as claimed in any of claims 1 to 13, **characterized in that** rinsing the goods is performed by using two or more rinsing stages in succession. 45
15. A method as claimed in claim 2, **characterized in that** the cleaning step comprises cleaning the goods in a cleaning system based on water which contains tensides and agents selected from organic and inorganic acids and alkali and alkaline earth hydroxides. 50
16. A method as claimed in claim 2, **characterized in that** the cleaning step comprises cleaning the goods in a biologically active cleaning system based on water which contains tensides and microorganisms and having a pH of not less than 8.5. 55



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## EUROPEAN SEARCH REPORT

Application Number  
EP 93 11 4683

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X,D	EP-A-0 309 432 (HAKANSSON L. A. H.)  * page 8, line 33 - page 8, line 24; claims 1,5,7-10; figure 3 * * page 10, line 11 - page 10, line 46 * ---	1,2,4,5, 7-11,13, 16	C23G5/00 C11D3/38
P,X	DE-A-42 09 052 (KUNZ P.) * claims 1,2,6,8-10,12,14; figures 4,5 * ---	1-4,16	
A	EP-A-0 424 340 (HAKANSSON L. A. H.) * claims 1,8,9 * ---	1	
A	DATABASE WPI Week 7429, Derwent Publications Ltd., London, GB; AN 74-53104V & JP-B-49 024 967 (MITSUI TOATSU CHEMS INC) 26 June 1974 * abstract * ---		
P,A	WO-A-92 16314 (HAKANSSON L.) -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 December 1993	Examiner Torfs, F
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

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